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(54) LIQUID INJECTION SEALING UNDERFILL MATERIAL

(57) Abstract:

PROBLEM TO BE SOLVED: To obtain a liquid injection sealing underfill material for semiconductor packages that does not cause exfoliation and cracks even in pressure cracker test and thermal cycle test.

SOLUTION: This liquid injection sealing underfill material contains, as main components, (a) a liquid epoxy resin, (b) an aromatic amine-based curing agent, an alkylated diaminodiphenylmethane, (c) a silane coupling agent having one or more functional groups selected from epoxy, amino and mercapto groups in one molecule, and (d) an inorganic filler having a specific particle size distribution, in such conditions that compounding ratios of respective components by weight is in relationships of (c)/[(a)+(b)+(c)]=0.01 to 0.05 and (d)/[(a)+(b)+(c)+(d)]=0.50 to 0.80, and that the inorganic filler has an average particle size of 4-6μm, and contains 20-70wt.% of particles of 1μm or smaller size, and 30wt.% or less of particles of 30μm or larger size up to 50μm, with larger particle sizes than 50μm cut out.

epoxy : amine
p.2 as low as 0.9 : 1
diluent ?

DERWENT-ACC-NO: 1998-393531

DERWENT-WEEK: 200281

TITLE: Liquid injection sealing under filler- contains liquid epoxy resin, alkylated diaminodiphenylmethane curing agent, silane coupling agent and inorganic filler

PATENT-ASSIGNEE: SUMITOMO BAKELITE CO LTD[SUMB]

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BASIC-ABSTRACT:

A liquid injection sealing under filler contains (a) liquid epoxy resin, (b) alkylated diaminodiphenylmethane as an aromatic amine type curing agent, (c) silane coupling agent which has epoxy, amino, and/or mercapto gp. as functional gp. and (d) inorganic filler as the main components. (d) has average particle dia. (average Dp) of 0.4-6 micron and contains 20-100 wt. % of particles having particle dia. (Dp) of 1 micron or less and 30 wt. % or less of particles having Dp of 20 micron or more and 0 wt. % of particles having Dp of 50 micron or more. A mixed ratio of (c)/[(a)+(b)+(c)] is 0.01-0.05 and (d)/[(a)+(b)+(c)+(d)] is 0.50-0.80.

USE - The under filler is used for injection-sealing a semiconductor.

ADVANTAGE - A semiconductor package sealed with the under filler has high reliability without release-cracking on pressure cooker test or a thermal shock test.

CHOSEN-DRAWING: Dwg.0/0

TITLE-TERMS: LIQUID INJECTION SEAL FILL CONTAIN LIQUID EPOXY RESIN ALKYLATED CURE AGENT SILANE COUPLE AGENT INORGANIC FILL

DERWENT-CLASS: A21 A85 L03

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2.**** shows the word which can not be translated.
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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the liquefied impregnation closure under-filling ingredient used for the impregnation closure of a semi-conductor.
[0002]
[Description of the Prior Art] With progress of the densification of IC chip, and high integration, a wire length is short and the par cage gestalt of the object for high frequency and the flip chip mounting method suitable for many pin-ization is increasing. This mounting is the magnitude of a chip size mostly, and since it can carry out direct loading of the chip at a printed circuit board, small, a light weight, and a thin shape are still more possible for it. Although the bare chip technique is also establishment-ized, since acquisition of a perfect excellent article chip is difficult, the restoration reinforcement by the impregnation closure under-filling ingredient is required.
[0003] Although the liquefied closure ingredient was used for this flip chip mounting mold semi-conductor closure, compared with the hermetic seal mold by the ceramics, it was not enough in respect of dependability, and the spread of plastic packages was behind compared with the dual in-line (henceforth DIP) mold. As a cause of a dependability fall of a flip chip mounting mold semi-conductor, the impurity from the open air by the lack of restoration of (1) impregnation closure under-filling ingredient and moisture invade.
(2) Moisture invades from an organic printed-circuit board.
(3) An impurity invades from a solder bump.
(4) In order to flow in a package and to harden a liquefied impregnation closure under-filling ingredient by the non-draft, when air bubbles remain and heat stress is added into a closure ingredient, a crack occurs.
(5) Since the coefficient of linear expansion of a closure ingredient, and a semiconductor chip, an organic substrate and a solder bump differs, when heat stress is added, exfoliation by the interface will be produced and invasion of moisture will be made easy.
(6) mechanical [to a chip] by this heat stress -- it will damage and loss will be produced. ** is mentioned.
[0004]
[Problem(s) to be Solved by the Invention] Then, the result to which examination was wholeheartedly come in piles in order that this invention persons might solve such a conventional problem, Liquefied epoxy resin and aromatic amine system curing agent alkylation diamino diphenylmethane, The constituent which blended with the silane coupling agent the unlimited filler which has specific particle size distribution It finds out becoming the package ingredient which can improve the dependability of a semi-conductor sharply also in accelerated tests, such as a pressure cooker test (henceforth PCT), and a cold energy cycle test (henceforth traveler's check), and comes to complete this invention.
[0005]
[Means for Solving the Problem] This invention (a) liquefied epoxy resin, (b) aromatic amine system

curing agent alkylation diamino diphenylmethane, (c) The silane coupling agent which has in intramolecular an epoxy group, an amino group, and one or more functional groups chosen from the group of a sulfhydryl group, In the liquefied impregnation closure under-filling ingredient which uses as a principal component the inorganic filler which has the particle size distribution of (d) specification the blending ratio of coal of each component by the weight ratio and by (c)/{(a)+(b)+(c)} =0.01-0.05 And it is (d)/{(a)+(b)+(c)+(d)} =0.50-0.80, and the mean particle diameter of the inorganic filler of (d) is 0.4-6 micrometers. Particle size of 1 micrometer The following among [all] an inorganic filler component at 20 - 100 % of the weight And particle size of 20 micrometers The above thing at 30 or less % of the weight in [all] an inorganic filler component It is the liquefied impregnation closure under-filling ingredient which blended the inorganic filler which has the particle size distribution which cut 50 micrometers or more, and the dependability of the flip chip mounting mold semi-conductor using an organic printed-circuit board can be raised sharply.

[0006]

[Embodiment of the Invention] As for the liquefied epoxy resin of (a) used for this invention, it is desirable 50% of the weight or more of the component of that the viscosity in 25 degrees C is 10 or less PA-s. Since air bubbles are involved in, or it will become easy to generate the short shot to a corner edge and will lead to a dependability fall in case the viscosity of a constituent becomes high and carries out inflow closure of under a flip chip mounting package with a liquefied impregnation closure under-filling ingredient if 50% of the weight or more of an epoxy resin component is not liquefied epoxy of hypoviscosity, it is not desirable.

[0007] In the case of a liquefied ingredient, as a viscosity measuring method of an epoxy resin, it measures in 25 degrees C with East Machine Industry and a ** E mold viscometer, and a Brookfield viscometer at a room temperature. If it is the epoxy resin with which are satisfied of this requirement and an example will be given although not limited especially Bisphenol A diglycidyl ether mold epoxy, bisphenol F diglycidyl ether mold epoxy, Bisphenol S diglycidyl ether mold epoxy, 3, 3', 5, 5'-tetramethyl - 4 4'-dihydroxybiphenyl-diglycidyl-ether mold epoxy, 4 and 4'-dihydroxybiphenyl-diglycidyl-ether mold epoxy, There are 1, 6-dihydroxybiphenyl-diglycidyl-ether mold epoxy, phenol novolak mold epoxy, bromine mold cresol novolak mold epoxy, bisphenol D diglycidyl ether mold epoxy, etc. These do not interfere, even if it mixes, even when it is independent. Moreover, in order to obtain the liquefied impregnation closure under-filling ingredient which was excellent in dependability, the fewest possible things of ionicity impurities, such as Na+ and Cl-, are desirable [the epoxy resin which is equal to use].

[0008] The aromatic amine system curing agent of (b) used for this invention is alkylation diamino diphenylmethane. The amines which do not have a ring are lacking in thermal resistance, since they are rich in reactivity also under the ambient atmosphere below nullity, have the fatal fault of being inferior to shelf-life, and are not suitable for this invention. Moreover, in order to obtain the liquefied impregnation closure under-filling ingredient which was excellent in dependability, the fewest possible things of ionicity impurities, such as Na+ and Cl-, are desirable [the amine system curing agent which is equal to use]. The aromatic amine system curing agent as used in the field of here is 3, 3', 5, and 5'-tetramethyl. - 4, 4'-diamino diphenylmethane, 3, the 3'-diethyl -4, 4'-diamino diphenylmethane, etc. are mentioned. As for the aromatic amine system curing agent of (b), an ingredient with a very sufficient fluidity can be offered with combination with (a) liquefied epoxy resin. Even if it flows in a package and makes it harden by the non-draft, air bubbles all cannot generate fluid faults, such as a void and being un-filled up, easily, either.

[0009] As for the combination mole ratio of the epoxy resin of (a) which is base resin, and the aromatic amine system curing agent alkylation diamino diphenylmethane of (b) which is a curing agent, 0.9-1.2 are desirable. When 0.9 or less curing agent is excessive, the superfluously unreacted amino group will remain and it leads to the fall of damp-proof fall and dependability. Conversely, if 1.2 or more, i.e., an epoxy resin, increase, hardening will become inadequate and it will lead to the fall of dependability.

[0010] As an inorganic filler (only henceforth a filler) of (d), a crystal silica, fused silica, etc. are used, for example. Although a configuration generally has the shape of a globular shape, the letter of crushing,

and a flake etc., in order to attain reduction-ization of coefficient of linear expansion and to raise the effectiveness by adding more fillers, a spherical inorganic filler is the best. As for an addition, (d)/{(a)+(b)+(c)+(d)} =0.50-0.80 are desirable. When it is less than 0.50, the reduction effectiveness of an above-mentioned coefficient of linear expansion is small, and if 0.80 is exceeded, the viscosity of the liquefied impregnation closure under-filling ingredient obtained as a result will become high too much, and since it is not practical use level, it is not desirable.

[0011] Moreover, it is possible by adjusting the particle size distribution of a filler to pull out flowability, such as viscosity, to the maximum extent. It is known that there is an inclination for viscosity to become low as the filler in which the filler which generally has the large particle size distribution of a range has a big particle size. However, although viscosity becomes low, the comparatively heavy filler of the filler which arranged only a big particle size of 50 micrometers or more for the purpose of hypoviscosity-izing of specific gravity is certainly depressed during hardening, and the so-called filler sedimentation from which a presentation ratio differs by the upper and lower sides of a hardened material occurs. Moreover, the point of not flowing into a slit is mentioned as a demerit using a filler with a big particle size. There is also an inclination of the package of the formation of many pin-ized space-saving, and the height between a substrate and a chip (Stand OFF) is becoming narrow. It is in such an inclination, a liquefied impregnation closure under-filling ingredient is flowed by the non-draft, and in order to fabricate so that there may be no fluid faults, such as a void and being un-filled up, particle size of a filler must be made small as much as possible. However, the fault by which a fluidity is spoiled also increases by making particle size small.

[0012] Then, mean particle diameter of a filler is made smaller than 0.4-6 micrometers and that of the conventional liquefied closure ingredient, and it is the particle size of 20 micrometers. By cutting 50 micrometers or more and making particle size small at 30 or less % of the weight in a solid-stowing material component, the above thing did not spoil a fluidity, either but became possible [being sewn and filled up with the gap of a chip and a substrate]. moreover -- in addition -- and a thing 1 micrometer or less can make it fill up with 20 - 100 % of the weight, and adjusting particle size distribution uniformly among a solid-stowing material component

[0013] Even if it uses additives, such as the catalyst for promoting other resin and reactions other than the aforementioned indispensable component if needed, a diluent, a pigment, an elastomer, a coupling agent, a flame retarder, a leveling agent, and a defoaming agent, it does not interfere with the liquefied impregnation closure under-filling ingredient ingredient of this invention.

[0014] As an elastomer, it is good, and the PO ** butadiene compound with which low stress-ized - and toughening are expected and which an epoxy group has, random copolymerization silicone denaturation epoxy, random copolymerization silicone denaturation phenol resin, or the polyolefine of epoxy group content is mentioned, and compatibility with the epoxy resin of (a) may combine independent or several sorts. Generally, since an elastomer lacks in compatibility with an epoxy resin, after it carries out impregnation hardening, it has the property in which a moldability falls for bleeding. However, the above-mentioned elastomer which has included the epoxy group in some molecules has compatibility, and in order to react in part with (b) of a curing agent and to construct a bridge, bleeding nature becomes good and is considered that it can also discover the reduction in stress, and toughening.

[0015] Although for example, KIC measurement is mentioned to for example, a three-point bending test and the check of toughening at the check of the reduction in stress, the result of having excelled in any result of a test can be obtained. This elastomer can pull out low stress nature - and toughness by adjusting that addition to the maximum extent. Although 0.1 - 1.0% of an addition is desirable among a full-liquefied impregnation closure under-filling ingredient, if there are than 0.1%, it cannot desire effectiveness of low stress-ized - and toughening, and becomes the cause which a surface crack occurs especially at the time of traveler's check, and leads to the defect of dependability. [few] Moreover, if [than 1.0%] more, compatibility with the epoxy resin of (a) will worsen and will cause an oil float and moldability fall of carrying out bleeding, on a package front face. With 3 rolls, 2 hot calender rolls, and a vacuum mixer, a liquefied impregnation closure under-filling ingredient carries out distributed kneading, carries out bottom degassing processing of a vacuum, and manufactures for example, each

component, an additive, etc.
[0016]
[Example] The example and the example of a comparison which show this invention below explain.
[Example 1]
Bisphenol female mold epoxy resin (equivalent 155, 1.6 Pa-s @25 degree C) 100 weight sections diethyl diamino diphenylmethane 21 weight sections methane base 21 weight sections glycidyl trimethoxysilane Three weight sections fused silica A The property of the used fused silica which is the 200 weight sections carbon black 1 weight section is shown in Table 1.
[0017]
[Table 1]
第1表

	シリカA	シリカB	シリカC	シリカD	シリカE	シリカF
平均粒径(μm)	0.8	2.8	4.9	9.7	5.5	5.0
1μm以下の重量%	60	45	30	27	15	25
1～20μm以下の重量%	35	42	45	46	72	35
20μm以上の重量%	5	13	25	27	13	40
50μm以上の重量%	0	0	0	0	0	2

[0018] Distributed kneading of the above-mentioned raw material was carried out with 3 rolls, bottom degassing processing of a vacuum was carried out, and the liquefied impregnation closure under-filling ingredient was obtained. After making it pour into a flip chip mounting package for 5 minutes on a 80-degree C heating plate using the obtained liquefied impregnation closure under-filling ingredient, it hardened at 120 degrees C for 1 hour, hardened in oven at 165 more degrees C for 2 hours, and the semiconductor package was obtained. Viscosity made the value what was measured by 5rpm with the BrookField mold viscometer (@25C). It is so bad that this value is high. If viscosity exceeds 500poise, the workability at the time of dispensing will worsen. Moreover, a CHIKISO ratio is the above-mentioned viscometer and made the value the ratio of the viscosity in 0.5rpm and 5rpm. Shelf life took the time amount which becomes twice initial viscosity. With the supersonic detector (henceforth C-SAM), exfoliation with the existence (it expresses by package restoration nature) of the void inside a package, a semiconductor chip side, and a printed circuit board bump interface and the existence of a crack were checked. When PCT processing (125 degree-C/2.3atm) and traveler's check processing (-65 degrees C / 30 minutes <- ->150 degrees C /, 30 minutes) were performed and exfoliation with a semiconductor chip and a printed circuit board interface and the existence of a crack were checked in SAT, such a phenomenon was not accepted at all to 1000 cycle traveler's check processing, but it became clear that it had good dependability for PCT processing 720 hours. The number of the flip chip mounting packages used for every evaluation is ten. In addition, a chip size is 15mm angle and the gap with a substrate is 100 micrometers. These evaluation results are shown in Table 2.
[0019] The liquefied impregnation closure under-filling ingredient was obtained like the example 1 except being based on combination of examples 2-5 and the [examples 1-5 of comparison] table 2. The semiconductor package was obtained like the example 1 using the obtained liquefied impregnation closure under-filling ingredient. These evaluation results are shown in Table 2.
[0020]
[Table 2]

第2表

(組成中の数値の単位: 重量部)

		実施例					比較例				
		1	2	3	4	5	1	2	3	4	5
ビスフェノールF型エポキシ樹脂		100	100	100	100	60	100	100	100	100	30
ナフタレン型エポキシ						40					70
ジエチルジアミノジフェニルメタン		21	42	42	42	47	21	42	42	42	45
テトラメチルジアミノジフェニルメタン		21					21				
グリシジルトリメトキシシラン		3	3	3	3	3	3	3	3	3	3
カーボンブラック		1	1	1	1	1	1	1	1	1	1
溶融シリカA		200	480			350				100	600
溶融シリカB				350							
溶融シリカC					350						
溶融シリカD							350				
溶融シリカE								350			
溶融シリカF									350		
粘度	ポイズ	200	450	390	310	420	500	620	310	70	1260
チキソ比	−	1.0	1.0	1.0	1.1	1.0	1.1	1.1	1.1	1.0	1.7
保存性	(○×△)	○	○	○	○	○	○	○	○	○	×
硬化性	ボイドの数	0	0	0	0	0	0	10	0	0	35
	未充填	0	0	0	0	0	5	3	0	0	20
	フィラー分離	なし	なし	なし	なし	なし	有	なし	有	なし	なし
硬化後	チップ面剥離	0	0	0	0	0	0	0	0	0	5
	バンプ面剥離	0	0	0	0	0	1	2	4	6	26
	クラック	0	0	0	0	0	0	0	0	27	0
PCT-720hr後	チップ面剥離	0	0	0	0	0	0	0	0	10	4
	バンプ面剥離	0	0	0	0	0	0	0	11	10	4
	クラック	0	0	0	0	0	0	0	0	6	2
T/C-1000サイクル後	チップ面剥離	0	0	0	0	0	0	1	0	0	0
	バンプ面剥離	0	0	0	0	0	24	0	3	0	4
	クラック	0	0	0	0	0	0	0	1	16	1

[(Naphthalene female mold epoxy resin (135 or 124 or less Pa-s [of equivalents] @25C)) 0021] [Effect of the Invention] If the liquefied impregnation closure under-filling ingredient of this invention performs the closure of a semiconductor package, since the semi-conductor of the high-reliability which does not have an exfoliation crack in a pressure cooker test or a cold energy cycle test can be obtained, it is industrial merit size.

[Translation done.]

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CLAIMS

[Claim(s)]
[Claim 1] (a) Liquefied epoxy resin and (b) aromatic amine system curing agent alkylation diamino diphenylmethane, (c) In the silane coupling agent which has in intramolecular an epoxy group, an amino group, and one or more functional groups chosen from the group of a sulfhydryl group, and the liquefied impregnation closure under-filling ingredient which uses (d) inorganic filler as a principal component The blending ratio of coal of each component by the weight ratio by (c)/{(a)+(b)+(c)} =0.01-0.05 It is (d)/{(a)+(b)+(c)+(d)} =0.50-0.80. The mean particle diameter and by 0.4-6 micrometers [an inorganic filler] A thing with a particle size of 1 micrometer or less is 20 - 100 % of the weight among [all] an inorganic filler component, and it is the particle size of 20 micrometers. Liquefied impregnation closure under-filling ingredient characterized by being the inorganic filler with which the above thing has the particle size distribution which cut 50 micrometers or more at 30 or less % of the weight in [all] an inorganic filler component.

[Translation done.]